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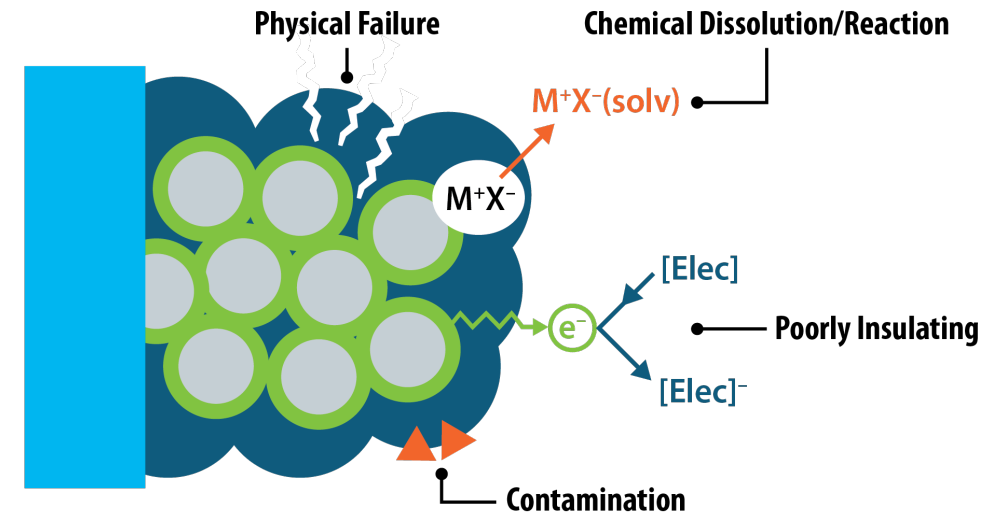
# THE SILICON CONSORTIUM PROJECT

*ADVANCED CHARACTERIZATION  
OF THE SI/SEI/ELECTROLYTE INTERFACES  
AND INTERPHASES*

**ROBERT KOSTECKI**

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“This presentation does not contain any  
proprietary, confidential, or otherwise  
restricted information”



# OVERVIEW

## Timeline

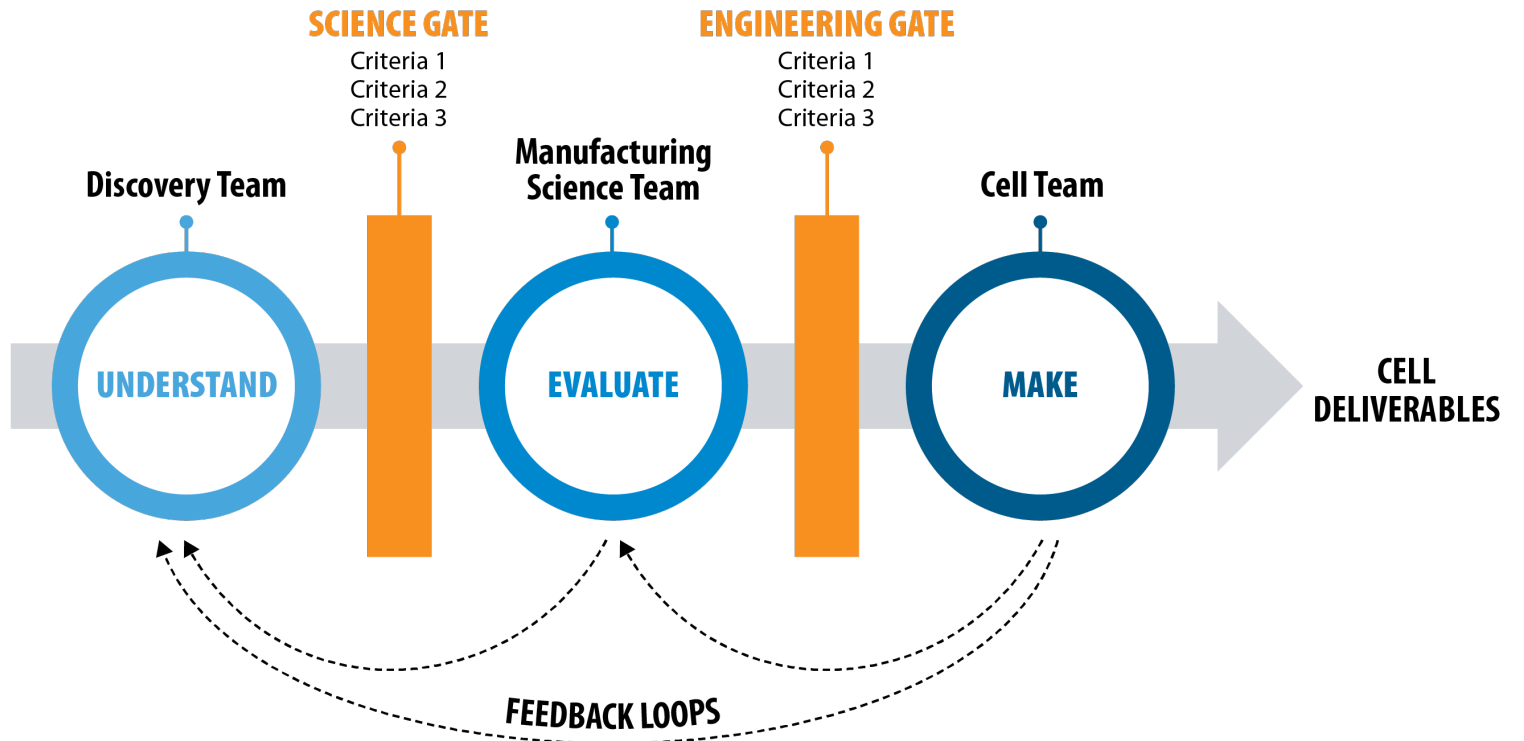
- October 1<sup>st</sup> 2020 - September 30<sup>st</sup> 2025.
- Percent complete: 10%

## Budget

- Funding for FY20: **\$7500K**

## Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals. Specifically targeting the development of calendar life in silicon anode.
  - Cost, Performance and Safety



# OUTLINE

## Timeline

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- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals. Specifically targeting the development of calendar life in silicon anode.
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## Research Thrusts

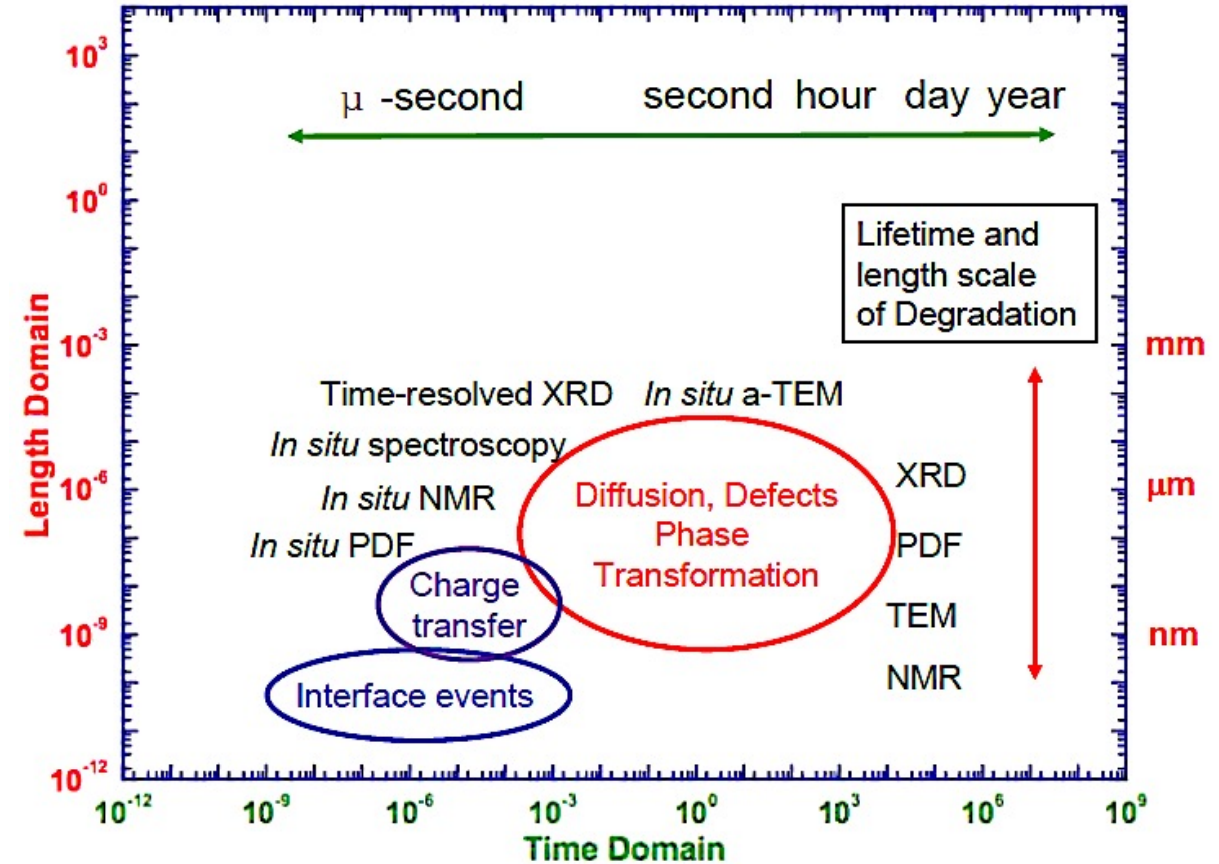
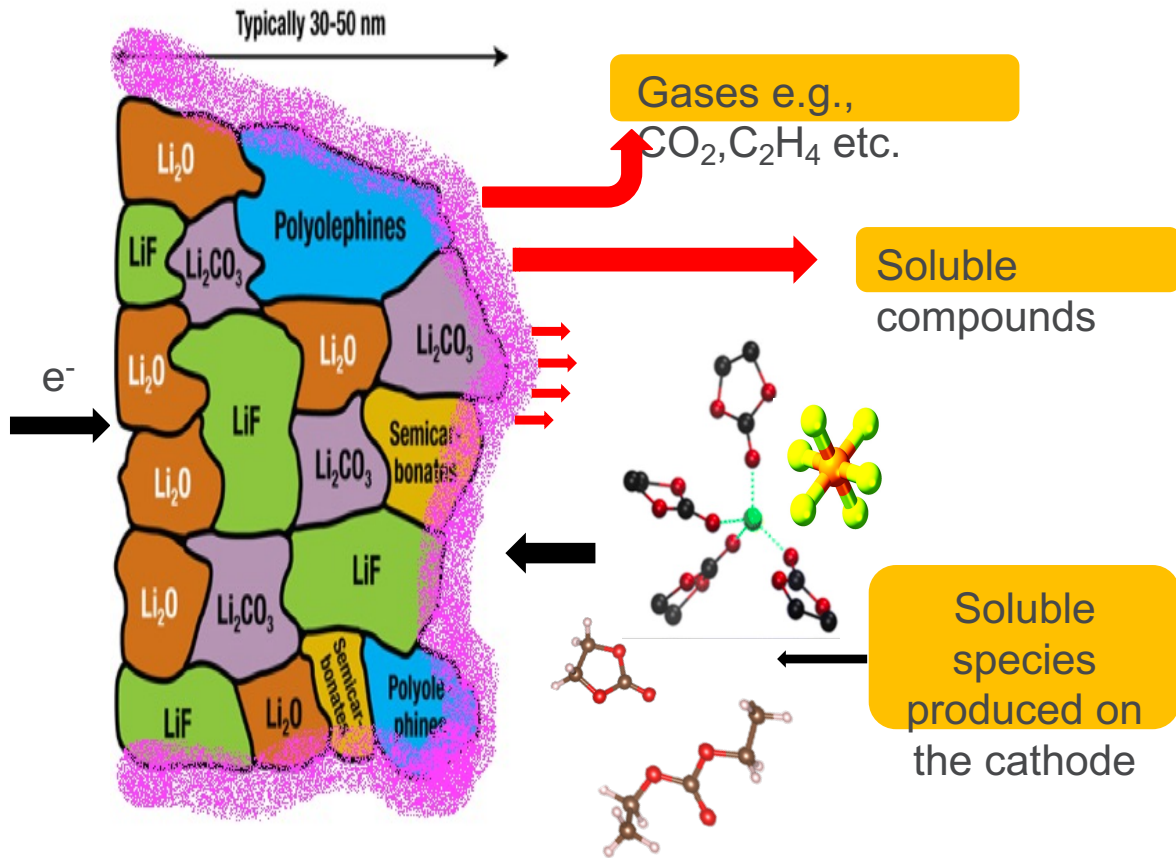
- Advanced characterization of the Si/SEI/electrolyte interfaces and interphases
- Electrochemical stability of the SEI
- Mechanical characterization of the SEI
- Next-generation materials discovery and development
- The science of manufacturing
- Cell manufacturing

# MILESTONES

- Establish a pre-lithiation protocol that can be utilized by all partners Q1 (complete)
- Go/no-go on HF etching of silicon oxide-silicon as viable route to silicon Q2 (complete)
- Go/No go on the Moire interferometry at as a method of probing the calendar life of the silicon SEI? Q3 (complete)
- Produce 20 grams of next generation silicon's with at least two different coatings, at least one of which exhibits enhanced calendar life over the baseline commercial silicon (NREL-centric) Q4 (on schedule)
- Advanced version of the calendar life protocols that quantifies calendar life in silicon-based anodes within 20% of the “real” calendar life predictions of calendar life. Q4 (on schedule)
- Synthesis and testing of 5 different metallic glasses with theoretical capacities  $> 1000$  mAh/g Q4 (on schedule)
- Identify active cell components and cell designs to achieve stable calendar life electrode performance with a cell build demonstrating 300 cycles with  $< 20\%$  capacity fade. Q4 (on schedule)

# SI/SEI/ELECTROLYTE CHARACTERIZATION CHALLENGES

Intrinsic non-passivating behavior of Si anodes in organic carbonate electrolytes



# SI/SEI/ELECTROLYTE CHARACTERIZATION CHALLENGES

## Intrinsic non-passivating behavior of Si anodes in organic carbonate electrolytes

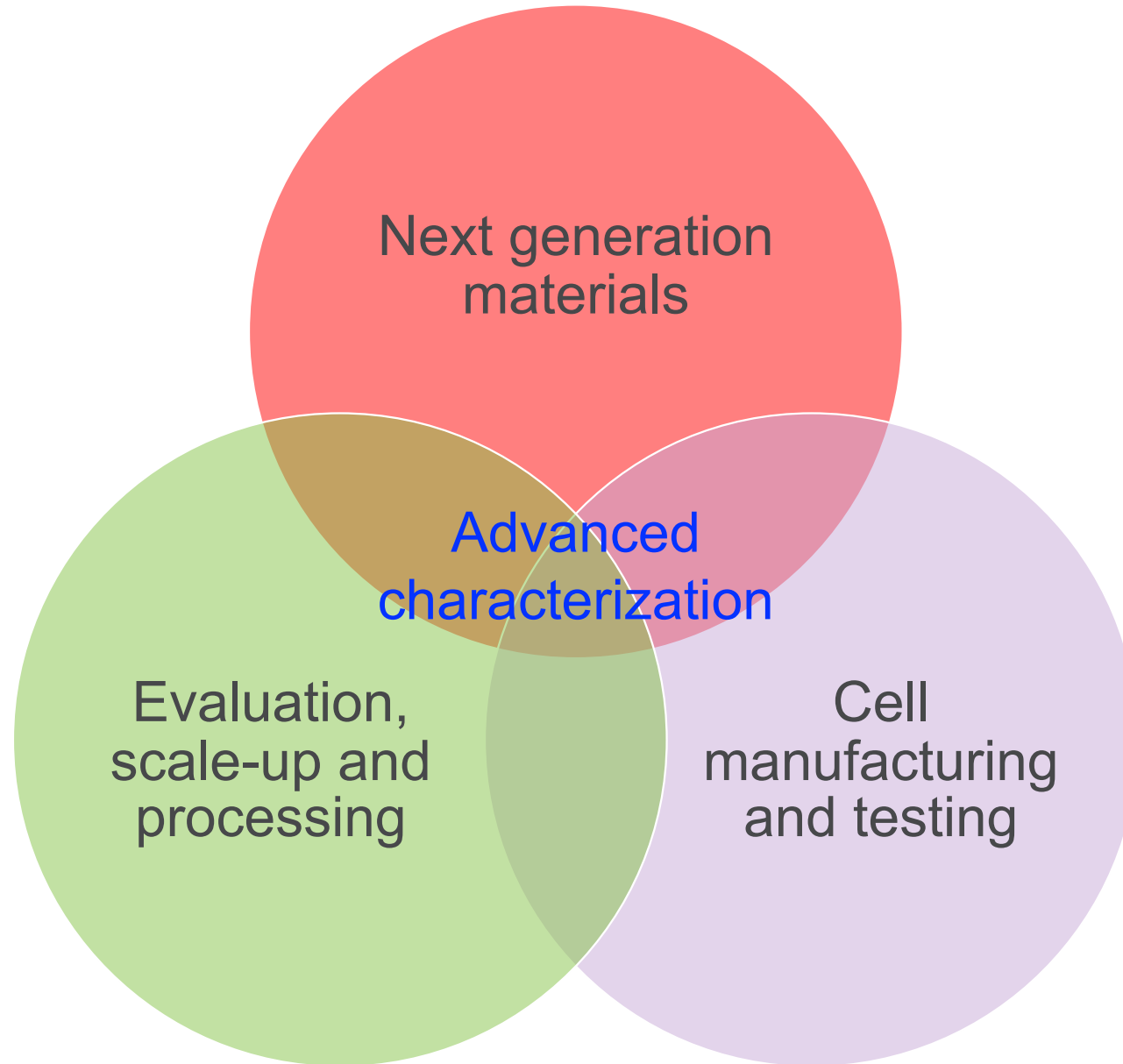
### I. Correlate physico-chemical properties of interfaces and interphases with unstable electrochemical behavior of Si electrode

- Electrode surface reactivity vs. SEI layer composition and structure
  - Design and study model electrodes with tailored interfaces to control the kinetics i.e., rate and selectivity of interfacial processes
- Unveil hidden SEI layer components and structures
- Understand the mechanism of SEI layer operation and function
  - Formulate working hypothesis of the mass and charge transfer across the surface film
  - Develop methods to track  $\text{Li}^+$  in the film and electrode active material
- Investigate chemical cross-talk effects between active and passive Si composite electrode components

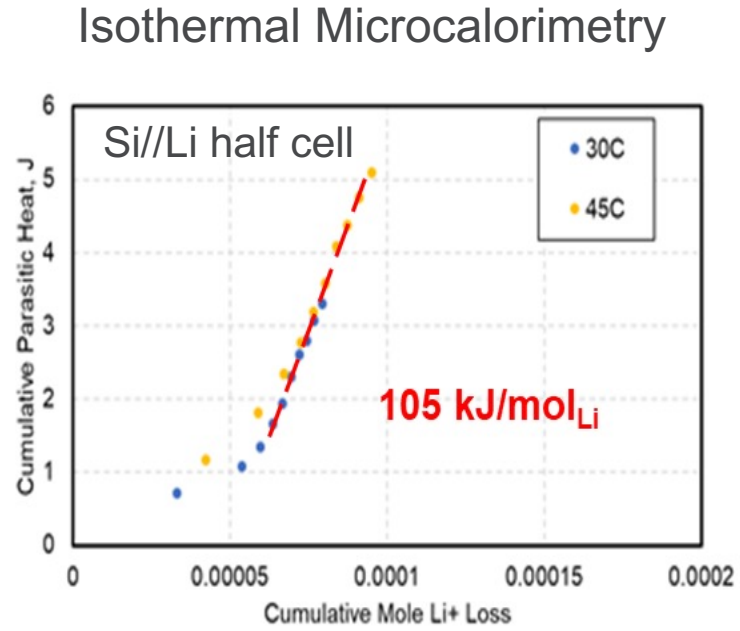
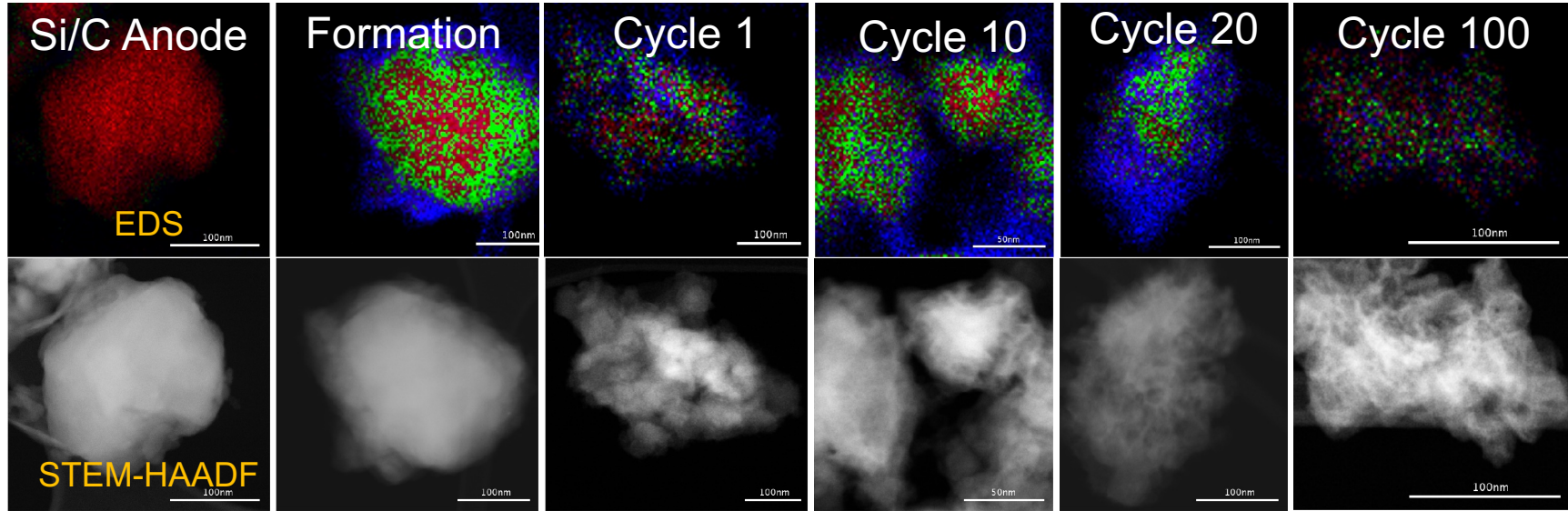
### II. Determine Si electrode design principles to address performance challenges

- Propose Si electrode modifications with regard to specific challenges, e.g., surface reactivity, electrochemical reactions kinetics, transport and mechanical properties etc.

# THE SILICON CONSORTIUM PROJECT



# NON-PASSIVATING BEHAVIOR OF SI IN ORGANIC CARBONATE ELECTROLYTES

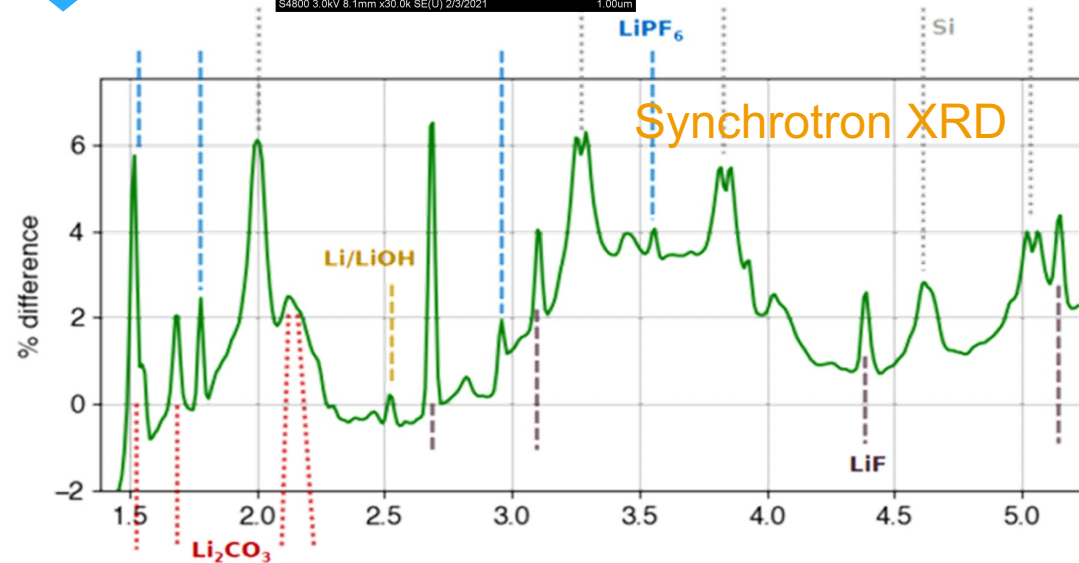
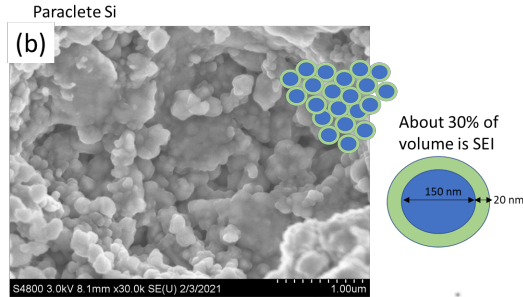


- With increased cycling number, Si particles decrepitate with pores filled with the electrolyte decomposition products
  - Local elemental analysis: Si = red, SEI (C, O, F, P, N) = blue, and Si/SEI = green
- Parasitic reactions enthalpies and corresponding heat flows confirm irreversible loss of Li and electrolyte over the lifetime of the cell

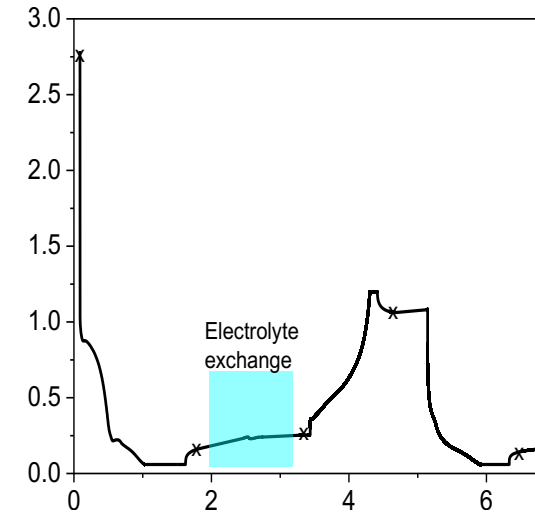
# SI ELECTRODE SURFACE REACTIVITY AND SEI COMPOSITION AND STRUCTURE I



Active material removed from cell and placed in capillary

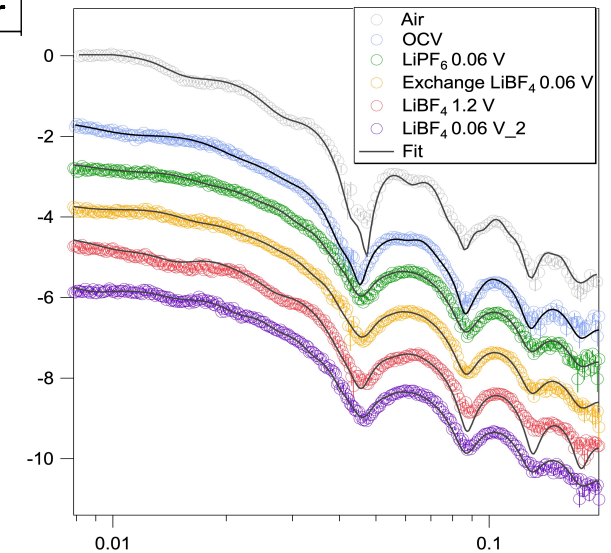


- SEI components include  $\text{Li}_2\text{CO}_3$ ,  $\text{LiF}$ ,  $\text{POF}_3$ , and  $\text{LiPF}_6$  (unidentified peaks still remain)
- Need to quantify mass fractions of crystalline SEI species for different stages of SEI (re)formation



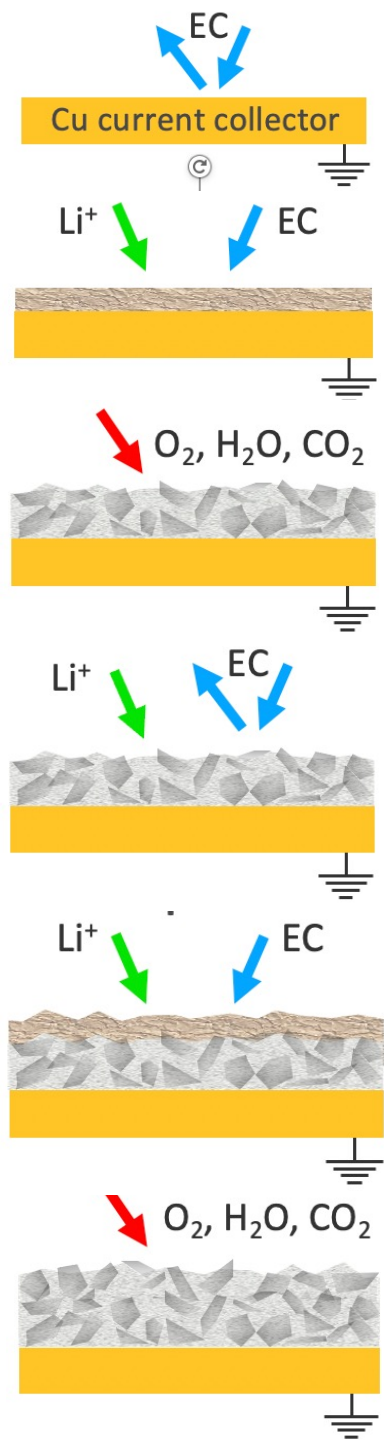
Electrochemical profile showing lithiation then exchange of electrolyte by adding boron tag

Neutron reflectivity spectroscopy reveals that  $\text{PF}_x$  component is easily removed from SEI with solvent exchange



Loss of  $\text{PF}_x$  in SEI layer enables self-discharge of the Si electrode

# SI ELECTRODE SURFACE REACTIVITY AND SEI COMPOSITION AND STRUCTURE II



Native point-defect calculations predict that increasing Li chemical potential increases electronic conductivity via  $Li_i^+$  shallow donor

Wang et al., npj Computational Materials 2018 4:15,  
Shi et al., J. Phys. Chem. C 2013, 117, 8579

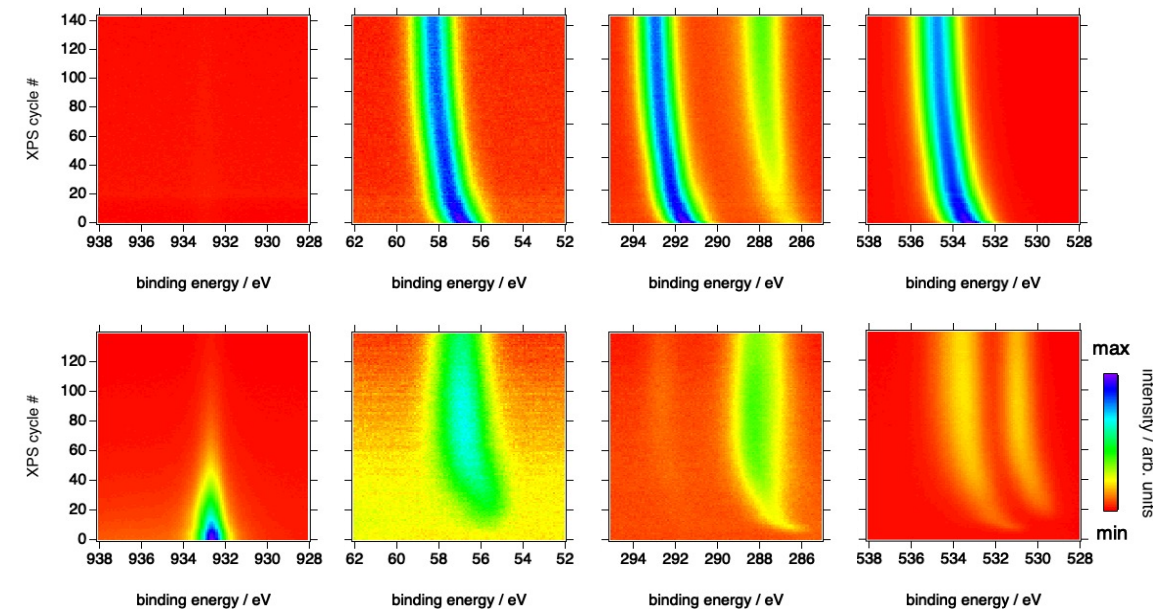
Similar effects might occur with other SEI constituents

Higher  $\mu_{Li}$  on  $Li_xSi$  vs.  $LiC_6$  anodes might be a root cause of poor calendar life.

*In situ* dosing with  $Li^+$  and EC enables tests of  $\mu_{Li}$  effects on electronic properties via binding-energy shifts

Li-organic phase(s) form on  $Li_2CO_3$  only after  $Li^+$  exposure increases its electrical conductivity.

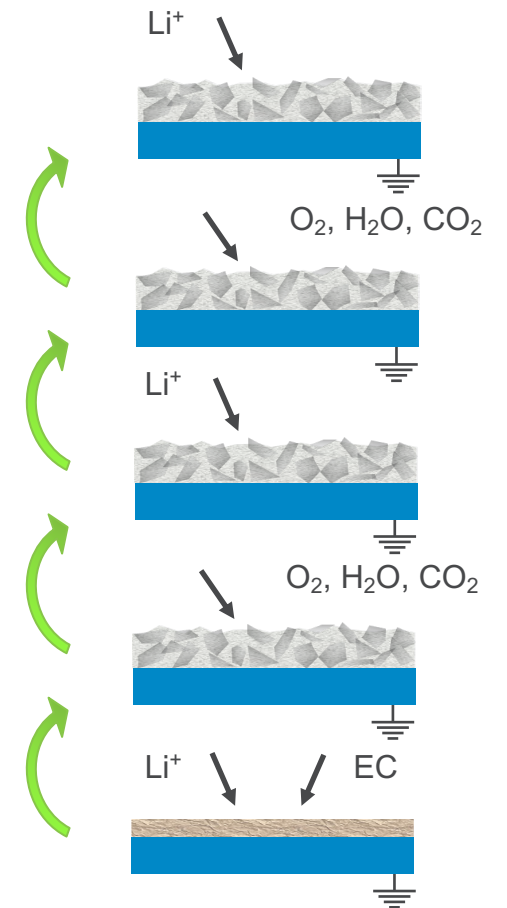
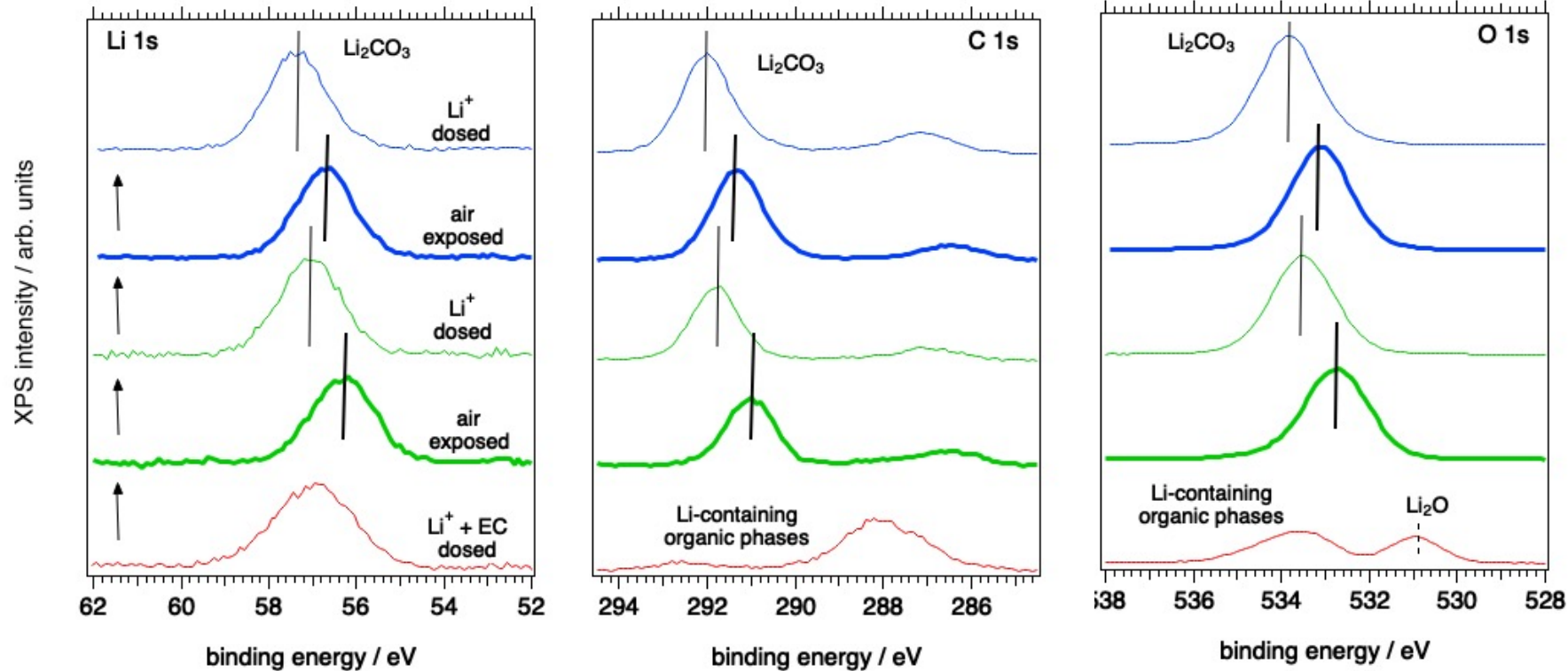
## XPS of Si Model Dosing System



- *In situ*  $Li^+$  + EC dosing forms Li-organics layer
- *Ex situ* air exposure converts film to  $Li_2CO_3$
- *In situ*  $Li^+$  + EC dosing probes  $Li_2CO_3$  conductivity;
- Li-organics growth begins ~ cycle 20

# SI ELECTRODE SURFACE REACTIVITY AND SEI COMPOSITION AND STRUCTURE III

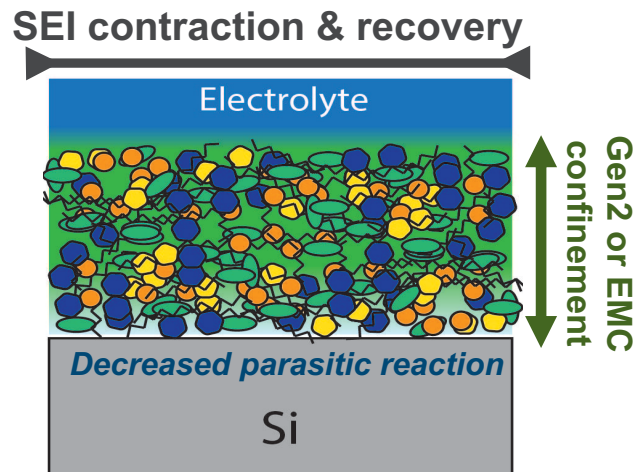
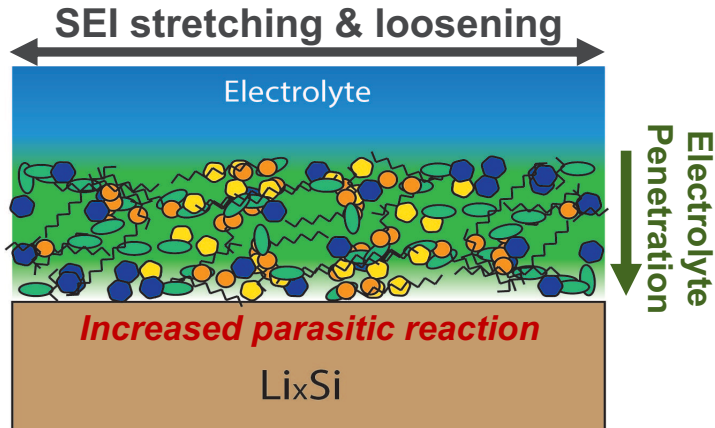
## XPS of Si Model Dosing System



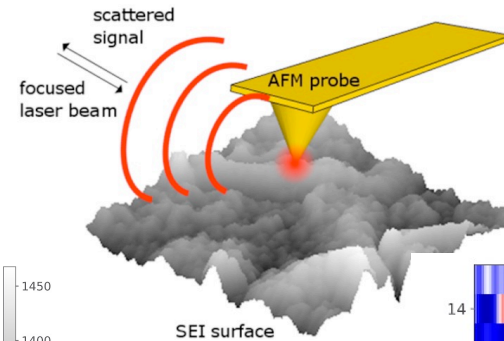
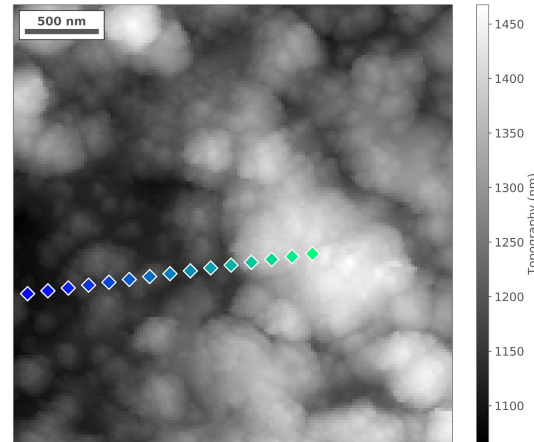
- $\text{Li}^+$  exposure raises  $m_{\text{Li}}$  and increases  $\text{Li}_2\text{CO}_3$   $e^-$  concentration (n-type doping)
- Subsequent air exposure re-oxidizes film, decreases  $e^-$  concentration

$\text{Li}_2\text{CO}_3$  becomes more conductive at high  $m_{\text{Li}}$  and facilitates electrolyte reduction

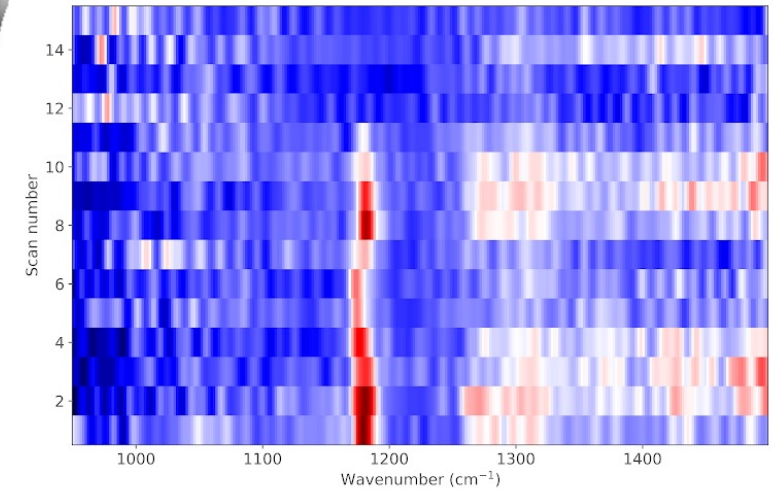
# SI ELECTRODE SURFACE REACTIVITY AND SEI COMPOSITION AND STRUCTURE IV



AFM topography



Nano-FTIR Spectra



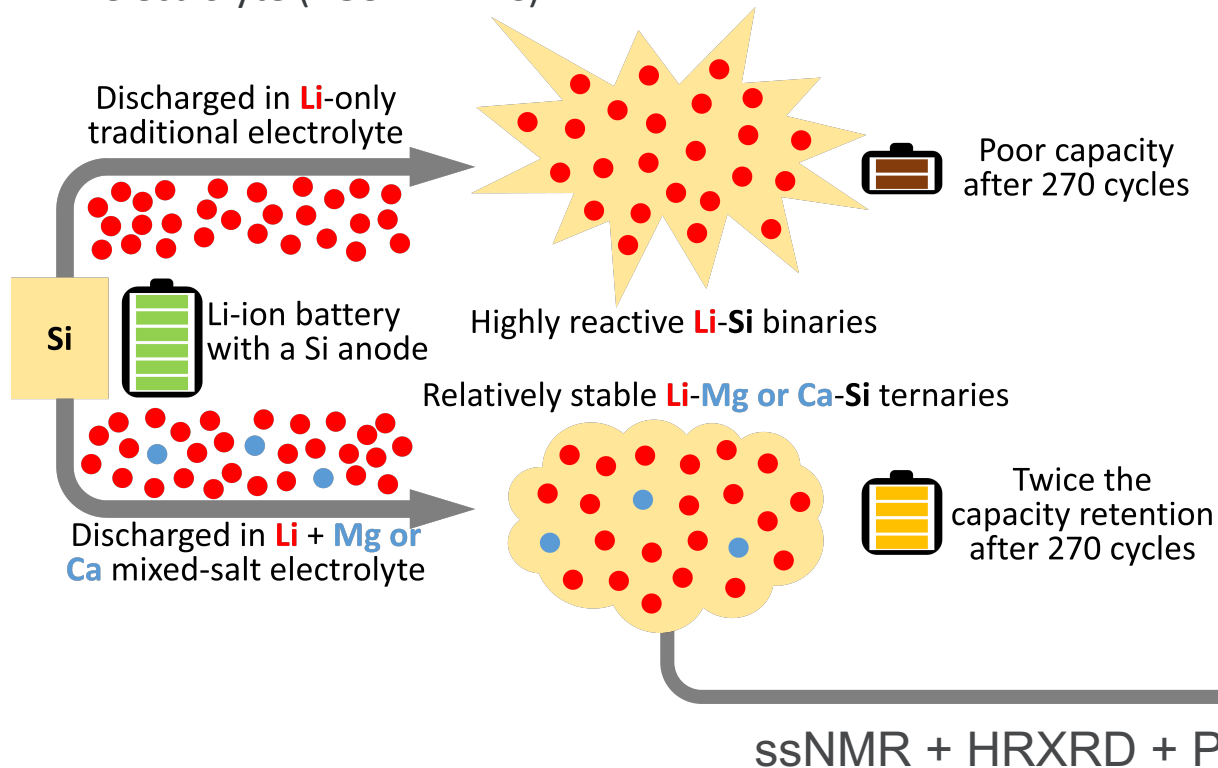
Nano-FTIR provides new insights in the origins of passivation instability caused by the SEI mechanical deformation upon lithiation/delithiation of Si

- EMC confinement in the SEI occurs during mechanical deformation of the surface film
- Nano-FTIR reveals inhomogeneous distribution of EMC in the SEI: EMC is trapped mostly in the thinner part of SEI.

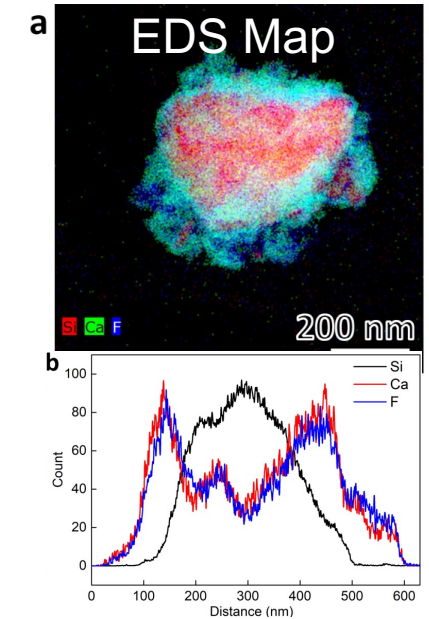
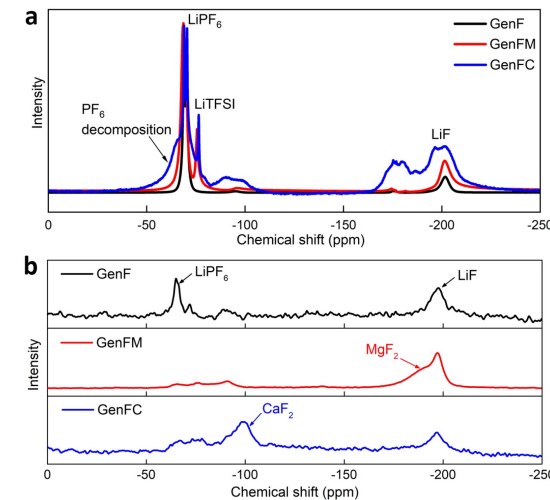
# NEW SI ELECTRODE DESIGN PRINCIPLES TO ADDRESS PERFORMANCE CHALLENGES I

## Ternary Zintl Phases to stabilize Silicon

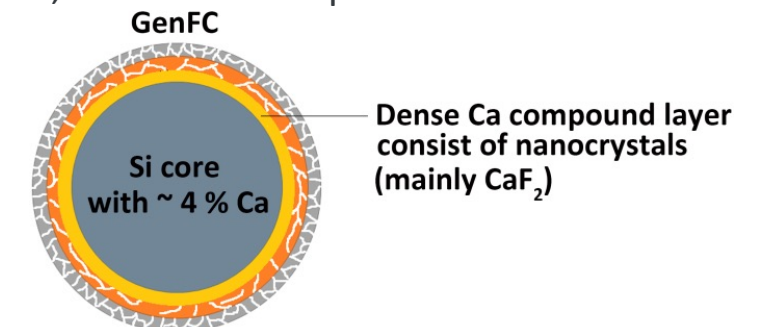
- More stable metal silicide phases formed via a simple salt additive to improve calendar life and cycle life
- 0.1M  $\text{Mg}(\text{TFSI})_2$  or  $\text{Ca}(\text{TFSI})_2$  additives, denoted as GenFM or GenFC formulations perform better over the baseline GenF electrolyte (=Gen2 + FEC)



## Solid State NMR



- $\text{CaF}_2$  (or  $\text{MgF}_2$ ) formation in addition to  $\text{LiF}$  produces a thinner and robust SEI layer
- Coupled with formation of *thermodynamically stable* ternary phases, the new SEI improves silicon calendar life



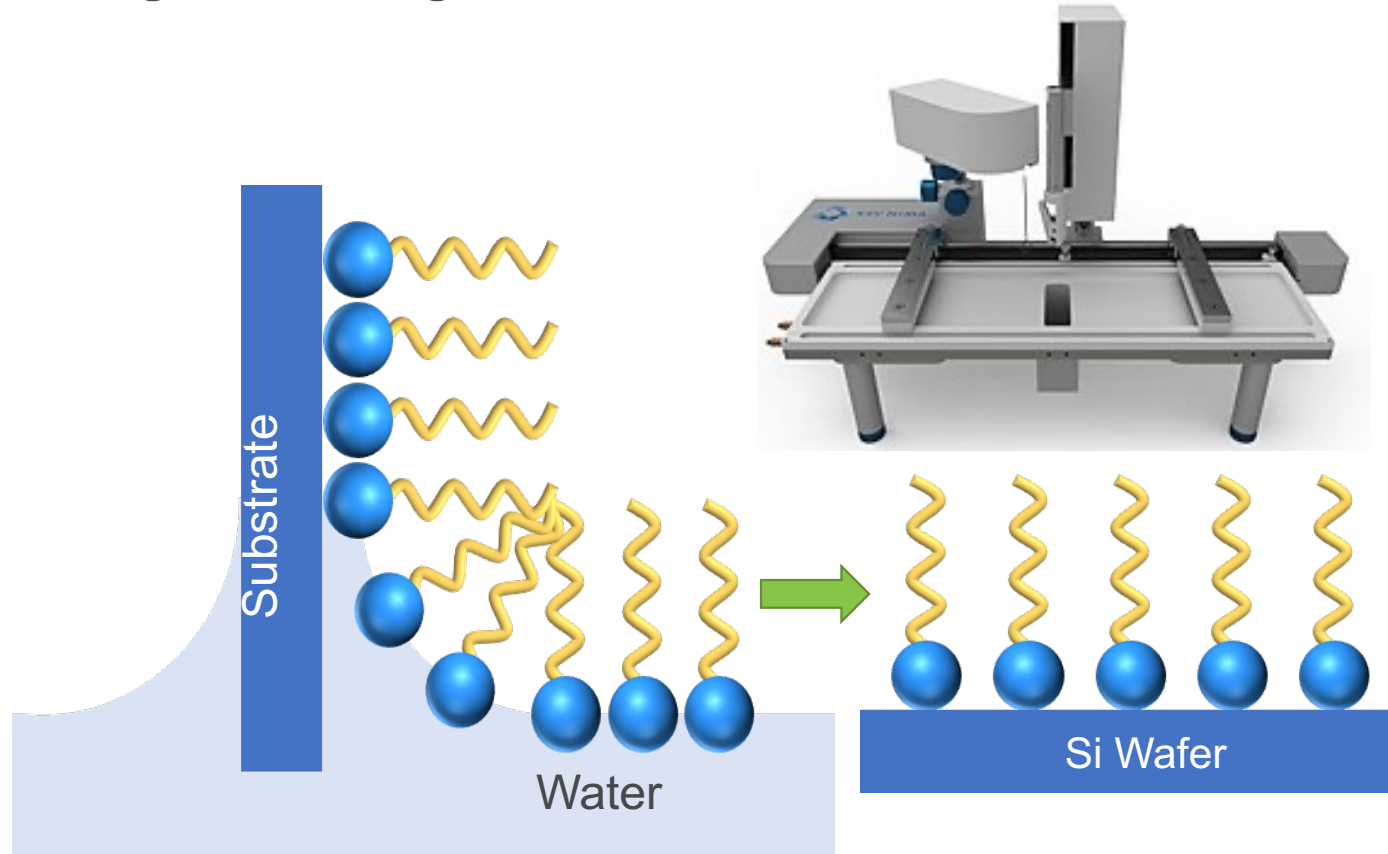
ssNMR + HRXRD + PDF + TEM + XPS

(See poster bat498)

# NEW SI ELECTRODE DESIGN PRINCIPLES TO ADDRESS PERFORMANCE CHALLENGES II

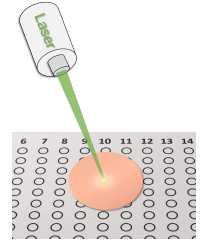
An ASEI presenting electrolyte-repellent surface and  $\text{Li}^+$ -permeable channels can properly passivate the electrode surface by minimizing electrolyte side reactions while maintaining  $\text{Li}^+$  conductivity

## Langumir-Blodgett surface film fabrication



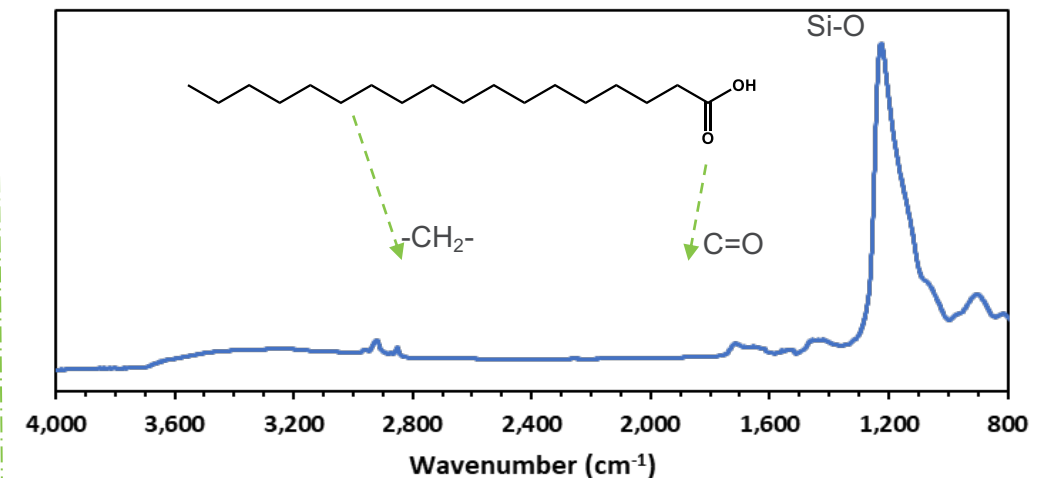
## Characterization

- STM/AFM
- FTIR/MALDI-TOF-MS
- CV/EIS/Cycling



MALDI is surface-compatible mass spectrometry method

## FTIR of 1 layer of Stearic Acid on Si wafer



# SUMMARY/ REMAINING CHALLENGES / FUTURE PLAN

I. Use round robin electrodes and model systems for control and modification of physico-chemical properties of SI/SEI/electrolyte interfaces and interphases

- Determine key controls of electrode surface reactivity, SEI layer composition and structure
- Understand the mechanism of SEI layer operation and function
- Correlate interfacial properties with electrochemical behavior

II. Develop and apply advanced characterization techniques, such as optical, X-ray, NMR spectroscopy and microscopy in combination with advanced electrochemical methods to determine function, operation and degradation of materials and Si electrodes in Li-ion battery cells.

III. Design rational Si electrode design principles to address performance challenges

- Correlate modifications to specific challenges, e.g. surface reactivity to electrolyte, volume change, “cracking, etc.
- Design and study model electrodes with tailored interfaces to control the kinetics i.e., rate and selectivity of interfacial processes.

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